Methanation of CO over Ni catalyst: A theoretical study*

William A. Goddard, III, Stephen P. Walch, Anthony K. Rappé, and Thomas H. Upton

Arthur Amos Noyes Laboratory of Chemical Physics,† California Institute of Technology, Pasadena, California 91125

Carl F. Melius‡

Sandia Laboratories, Livermore, California 94550

(Received 3 December 1976)

Theoretical methods (generalized valence-bond calculations) were used to examine the bond energies and geometries of numerous species chemisorbed onto Ni clusters representing Ni surface. These results were used to obtain thermochemical information and to examine various mechanisms for the methanation of CO over Ni: $CO+3H_2 \xrightarrow[(Ni)]{} CH_4+H_2O$. It is found that chemisorbed formyl radicals (Ni–CHO) lead to a favorably appearing chain reaction that is consistent with current experimental results. In addition, we find a chemisorbed C_2 species that may be the catalytically active C_{ad} formed from dissociation of CO.

PACS numbers: 82.65.My

I. INTRODUCTION

With the objective of examining various mechanisms for the methanation of CO over Ni,[1]

$$CO + 3H_2 \xrightarrow[(Ni)]{} CH_4 + H_2O, \qquad (1)$$

we carried out theoretical studies of the geometries and bond energies of numerous likely intermediates, chemisorbed on Ni. From these results we examined the energetics of a number of mechanisms of which two seem particularly favorable. One involves a reaction chain carried by chemisorbed formyl radicals; the other involves surface carbon from decomposed CO.

In order to obtain reliable bond energies, it is essential to include electron correlation effects. This is accomplished using the *ab initio* generalized valence bond (GVB) method,[2] in which the dominant electron correlation effects are solved for self-consistently, followed by an additional configuration interaction (CI) among the GVB orbitals. This approach leads to bond energies good to several kcal/mole.[3] Such *ab initio* calculations require a finite number of atoms, and we have in all cases replaced the semi-infinite Ni surface with a few Ni atoms. These calculations are simplified by replacing the Ar core of the Ni with an effective potential based on *ab initio* wave functions of the atom.[4] All calculations use a double-zeta contracted basis based on the Wachters[5] basis for Ni and the Huzinaga–Dunning basis[6] for H, C, and O. In most cases *d*-polarization functions were included on the first-row atoms.

Use of a finite complex to represent the surface results in several errors, some of which tend to underestimate the bond energy for chemisorption (the finite complex cannot polarize sufficiently in order to transfer enough charge to or from the adsorbate) and some of which tend to overestimate the bond energy (due to insufficient accounting for disruption of the metal–metal bonds). For example, chemisorption of H_2 onto Ni leads to[7] $\Delta H = -22.7$ kcal/mole, corresponding to an Ni–H bond energy of 63.4 kcal/mole, whereas we calculate that the diatomic molecule NiH ($^2\Delta$) has a bond energy of

$$D_0(\text{Ni–H}) = 63.6 \text{ kcal/mole}.$$

Similarly, chemisorption of CO onto Ni (111) leads to[8] $\Delta H = -26.5$ kcal/mole, whereas we calculate that

$$D_0(\text{Ni–CO}) = 26.4 \text{ kcal/mole}.$$

Our conclusion is that there is a balance of errors so that even the gross approximation of replacing the solid by a single Ni atom leads to reasonably good bond energies. (Note: based on careful studies of nontransition metal systems, we do not expect our calculated bond energies to be more accurate than 2 to 5 kcal/mole, and hence the excellent agreement of 0.2 kcal in the above cases must be considered accidental.)

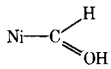
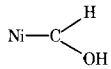
As a first pass at examining the energetics for a number of possible mechanisms, we have taken the following approach. We examined a number of adsorbates bonded to a single Ni and a number bonded to a pair of Ni in a bridged configuration,[16] and we assumed that the calculated bond energies are equal to the chemisorption energies for the corresponding sites of the Ni surface. In examining mechanisms it is generally the relative bond energies for various adsorbates on the same site that are most important, and we expect these quantities to be reasonably accurate.

II. RESULTS

Table I summarizes a number of our results, including some geometric information. For purposes of examining the reaction steps, we have converted the bond energy to a standard heat of formation ΔH_f for each chemisorbed species. Note that this number ignores interactions with any other chemisorbed species.

For example, the Hamai–Eidus mechanism[1] leads to the energetics in Fig. 1(a) if only single Ni sites are available and to the energetics in Fig. 1(b) if bridged sites are available. The first step in Fig. 1(a) is much too endothermic (49 kcal/mole)

TABLE I. Results from GVB–CI calculations. D_0 is the bond energy, ΔH_f is the standard heat of formation of the chemisorbed intermediate, R_{NiX} is the bond length to the Ni, Q is the charge transfer,[a] and ν_{MX} is the calculated vibrational frequency.

	D_0 (kcal/mole)	ΔH_f (kcal/mole)	R_{NiX} Å	Q electrons	ν_{MX} (cm^{-1})
Ni-H	64	−12	1.45	0.12	1911
Ni-CO	27	−53	1.90	−0.05	428
	34	−60	1.94	0.59	286
Ni=CH_2	65	27	1.78	0.56	1181
	122	−30	1.91	0.70	
Ni-CH_3	60	−25	1.87	0.42	1066
	57	−47		0.30	
	56	−4		0.36	
	91	80			
Ni=O	91	−31	1.60	0.55	838
	101	−41	1.79	0.91	170
Ni-OH	50	−41	1.72		
Ni=S	76	−9	1.91	0.38	483
	124	−57	2.04	0.57	297

[a]This is from Mulliken populations and need not be a good measure of total charge transfer.

to be considered further. This problem is avoided in the bridged case, Fig. 1(b); however, the rate-determining step (RDS) in this mechanism would seem to be the third step, which seems inconsistent with experimental kinetics.[9,10]

A. The formyl chain mechanism

From Fig. 2(a) we see that there are exothermic processes in which chemisorbed formyl radicals are formed from chemisorbed CO or H_2. In Fig. 2(b) we see that with chemisorbed formyl radicals present one obtains a series of exothermic steps constituting a chain reaction for producing CH_4 while regenerating the formyl radical.[11] In this chain it is step b1 that is most likely to be the RDS. Assuming that the normal chemisorption sites are saturated with CO (as expected from the differential bond energies) and assuming that the H_2 in step b1 is in a weakly bound site nestled between strongly chemisorbed species, leads to a rate expression of the form

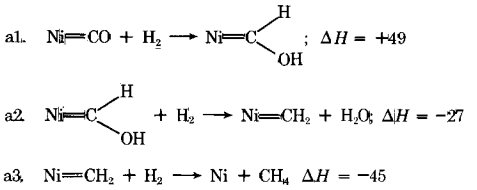
$$R_{CH_4} = \frac{k(P_{H_2})^{3/2}}{1 + K_1 P_{CO} + K_2 P_{H_2}}. \tag{2}$$

Rewriting this in the form

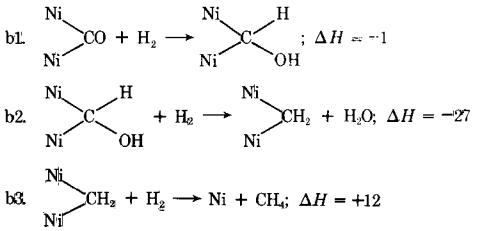
$$R_{CH_4} = \bar{k}(P_{H_2})^a (P_{CO})^b, \tag{3}$$

FIG. 1. The Hamai–Eidus mechanism (all numbers in kcal/mole)

a. Linear site



b. Bridged site



the exponents must be in the range

$$\tfrac{1}{2} \le a \le \tfrac{3}{2},$$
$$-1 \le b \le 0. \tag{4}$$

The experimental results of Vannice[9] lead to $a = 0.77$ and $b = -0.3$ for Ni and lead to

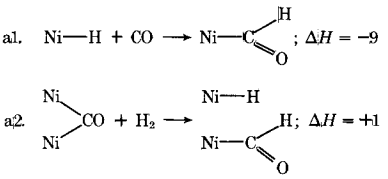
$$0.77 \le a \le 1.6,$$
$$-0.6 \le b \le 0.10 \tag{5}$$

for the set of group VIII metals[9] (Os not considered).

The above results do not of course prove that the formyl chain mechanism is responsible for methanation of CO. Some recent evidence in favor of a role for formyl radicals in catalyzing the production of CH_4 from CO can be read into the results of Madey *et al.*,[12] in which they introduced H_2CO into a CO and H_2 system producing CH_4 in steady state. Since the formyl chain mechanism requires only one metal atom, it could also play a role in related homogeneous reactions.

FIG 2. The formyl chain mechanism

a. Generation of Formyl Radicals



b. The Chain Process

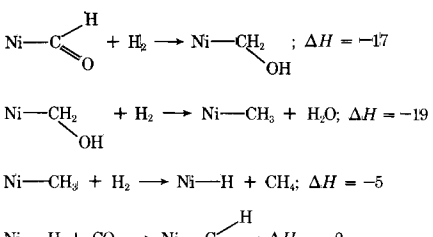
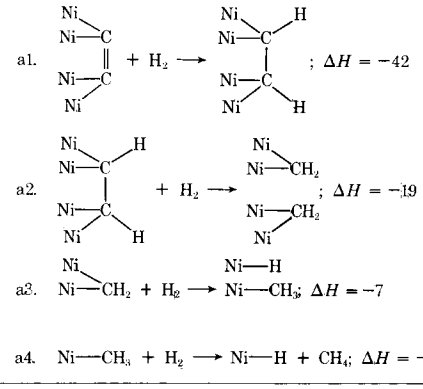


FIG. 3. Methanation of C_2 carbide



B. Surface carbide

It has been shown that heating chemisorbed CO (on Ni) above 450 K leads to dissociation of the CO into chemisorbed C and O species.[13] At sufficiently high temperatures (615 K) the C_{ad} converts to graphite; however, if kept at lower temperature, it has been recently shown[14] that the C_{ad} can be quantitatively converted into CH_4 by introduction of H_2.

Assuming the O_{ad} to be bonded in a bridge site on the surface, the energy for CO_{ad} going to graphite on Ni plus O_{ad} is 12-kcal endothermic. We will assume then that the final form for O_{ad} is a more stable site, perhaps slightly inside the surface, and we will take this extra bonding of the $\overline{O}_{ad}$ to be 15 kcal (to fit approximately the experimental conditions for converting to graphite). Combining our previous results into a thermochemical scheme analogous to the group function approach of Benson,[15] we obtained the following results. Assuming that C_{ad} is not graphite but an isolated C atom bonded to three Ni results in $\Delta H = 16$ kcal for

$$CO_{ad} \rightarrow (C_1)_{ad} + \overline{O}_{ad},$$

from which we conclude that the nongraphitic C_{ad} is *not* monatomic. On the other hand, we find that a C_2 species is strongly bonded to four Ni in a distorted ethylenic type structure leading to $\Delta H = +2$ kcal for

$$CO_{ad} \rightarrow \tfrac{1}{2}(C_2)_{ad} + \overline{O}_{ad}.$$

We did not find a similarly stable C_3 or C_4 species and conclude that the catalytically active C_{ad} may be such a C_2 species. Considering the subsequent attack of H_2 on this species leads to the results in Fig. 3. All steps are exothermic and this mechanism appears plausible.

III. SUMMARY

We envision two important roles that theory is likely to play in understanding chemical processes on surfaces. One is the development of qualitative concepts for visualizing and predicting the specific bonding interaction of adsorbates with surface sites. The GVB method was developed for just such purposes, but in the interest of brevity such illustrations have been omitted. The second role of theory is to provide quantitative data that are difficult to obtain from experiment. Examples of this are the geometries and binding sites of chemisorbed molecules and, more importantly, the bond *energies* of these molecules. It is this latter goal, the thermochemistry, to which we have addressed ourselves here. Currently there is so little reliable thermochemical information on related transition-metal systems that thermochemical arguments are seldom made in examining such mechanisms. Our current results, although crude, provide, we believe, enough information to begin application of thermochemistry in assessing mechanisms. We are currently in the process of extending these studies to other metals and to bigger clusters.

*Supported by a grant (DMR74-04965) from the National Science Foundation.
†Contribution No. 5472.
‡Supported by a contract from the U.S. Energy Research and Development Administration.

[1]V. M. Vlasenko and G. E. Yuzefovich, Russian Chem. Rev. **38**, 728 (1969); G. A. Mills and F. W. Steffgen, Catal. Rev. **8**, 159 (1973).
[2]W. A. Goddard III, T. H. Dunning, Jr., W. J. Hunt, and P. J. Hay, Acc. Chem. Res. **6**, 368 (1973).
[3]B. J. Moss and W. A. Goddard III, J. Chem. Phys. **63**, 3523 (1975).
[4]C. F. Melius, B. D. Olafson, and W. A. Goddard III, Chem. Phys. Lett. **28**, 457 (1974); M. J. Sollenberger, Masters thesis (California Institute of Technology, 1975).
[5]A. J. H. Wachters, J. Chem. Phys. **52**, 1033 (1970).
[6]T. H. Dunning, Jr., J. Chem. Phys. **53**, 2823 (1970).
[7](a) J. Lapujoulade and K. S. Neil, J. Chem. Phys. **57**, 3535 (1972); Surf. Sci. **35**, 288 (1973); (b) K. Christmann, O. Schober, G. Ertl, and M. Neumann, J. Chem. Phys. **60**, 4528 (1974); (c) The experimental results are $\Delta H = -22.7$ kcal/mole for Ni (111) and $\Delta H = -23.1$ for Ni (100) from (a) and $\Delta H = -22$ from (b).
[8]K. Christmann, O. Schober, and G. Ertl, J. Chem. Phys. **60**, 4719 (1974).
[9]M. A. Vannice, J. Catal. **37**, 449, 462 (1975).
[10]For other recent work see also R. A. Dalla Betta, A. G. Piken, and M. Shelef, J. Catal. **40**, 173 (1975); P. Schoubye, *ibid.* **14**, 238 (1969); T. Van Herwijnen, H. Van Doesburg, and W. A. De Jong, *ibid.* **28**, 391 (1973).
[11]J. L. Bousquet, P. C. Gravelle, and S. J. Teichner [Bull. Soc. Chim. Fr. 3693 (1972)] have also suggested that a formyl radical may possibly be involved in methanatic.
[12]T. E. Madey, J. T. Yates, Jr., and R. D. Kelley, paper presented at the American Chemical Society's National Meeting in San Francisco, California, August 29–September 3, 1976.
[13]J. E. Tracy, J. Chem. Phys. **56**, 2736 (1972).
[14]H. H. Madden and G. Ertl, Surf. Sci. **35**, 211 (1973); P. B. Tottrup, J. Catal. **42**, 29 (1976); P. R. Wentrcek, B. J. Wood, and H. Wise, J. Catal. **43**, 363 (1976); P. R. Wentrcek, J. G. McCarty, B. J. Wood, and H. Wise (unpublished).
[15]S. W. Benson, *Thermochemical Kinetics* (Wiley, New York, 1968).
[16]The Ni of the bridge were taken as second nearest neighbors, as appropriate for (100) or (110) surfaces.